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MAGNESIUM OXYCHLORIDE CEMENTS

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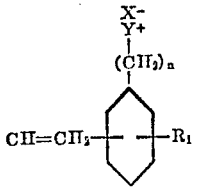
The present invention relates to magnesium oxychloride cements having improved wet strength characteristics. More particularly, the invention concerns magnesium oxychloride cements containing a minor proportion of a polymeric polysulfonium composition.

Magnesium oxychloride cements are made by mixing calcined or caustic magnesia (magnesium oxide), a suitable filler or aggregate and an aqueous solution of magnesium chloride which is frequently termed "a gauging solution." Upon being thoroughly mixed in suitable proportions, these materials form a plastic mass which may be cast, poured, molded, extruded, pressed or foamed, depending upon the relative quantities of the constituents, special additives and the type of aggregate employed to provide a wide variety of useful articles. When exposed to air, with or without the aid of heat, the shaped plastic mass dried into a hard cement. These cements, which otherwise exhibit highly desirable properties, deteriorate upon continuous or intermittent exposure to water, thus rendering the cement inapplicable for uses where good weathering properties are an important criterion. This problem has been the subject of extensive investigation in the art and as a result numerous additives have been proposed to improve the moisture resistance or wet strength of magnesium oxychloride cements. The advantages resulting from the use of such additives, as have been proposed, have varied widely in effectiveness and economic practicality.

It is, therefore, desirable and among the objects of the present invention to provide novel additives for magnesium oxychloride cements capable of minimizing water-induced deterioration of the cement. It is especially an object of the invention to provide such an additive which is effective in relatively low concentrations. A further object is to provide such an additive which can be effectively incorporated into cured or set magnesium oxychloride cements. A still further object is to provide an improved magnesium oxychloride cement composition having improved resistance to the degradative action of water. Other objects and benefits will become manifest hereinafter as the invention is more fully described.

In accordance with the present invention, it has been discovered that the resistance of magnesium oxychloride cements to the deleterious influence of water is substantially improved by incorporating into the cement a minor proportion, for example, at least about 0.02 and up to an effective upper limit of about 3 percent by weight of the cement, of a water-soluble polymeric polysulfonium composition containing in chemically combined form at least a substantial proportion of a monomer having the following general formula:



wherein R_1 is selected from the group consisting of hydrogen, halogens and alkyls having up to 6 carbon atoms, Y is a divalent, sulfur-containing, organic radical having its valences on the sulfur atom, said radical being derived from aliphatic and cycloaliphatic organic sulfides having

from 2 up to 12 carbon atoms, X is a counter anion, preferably a halide such as chloride or bromide, and n is an integer from 1 to 4.

More particularly, Y corresponds to the following formula

wherein R_2 and R_3 separately represent monovalent radicals such as, for example, alkyls, haloalkyls, hydroxyalkyls, carboxyalkyls, acyloxyalkyls, carboalkoxyalkyls, carbamoylalkyls, alkylcarbamoylalkyls, alkylamidoalkyls and

$$(C_aH_{2a}Z)_bC_aH_{2a}$$

radicals wherein Z is selected from the group consisting of oxygen and sulfur, a is an integer from 2 to 4, b is at least 1, said monovalent radicals having from 1 up to 12 carbon atoms. Taken together, R_2, R_3 and S represent a cyclic, saturated organic sulfide radical having from 4 to 6 ring carbon atoms which may contain substituents such as halogen, alkyl, amino, hydroxyl and the like groups.

Normally, the above-described sulfonium compounds, as produced, will have a halide counter anion. If desired, however, the halide form of the sulfonium group can be converted in a conventional manner to any one of a number of common anionic forms such as carbonate, nitrate, sulfate, acetate and the like by passing a solution of the monomer or polymer in which it is combined through an anion exchange resin bed in the proper salt form.

The preferred polymeric polysulfonium additives of the invention correspond to homo- and copolymers of the above-described monomeric materials. However, some benefit in accordance with the invention is obtained with any water-soluble polymer corresponding to a copolymer of the above-described sulfonium substituted monomers and other ethylenically unsaturated hydrophobic and/or hydrophilic monomers, which polymer contains at least a substantial proportion of the sulfonium substituted monomeric materials, e.g., at least about 20 percent of the total combined monomers. Note that while lesser amounts of the hydrophilic sulfonium substituted monomers can be employed with other comonomers to prepare the water-soluble polymeric additives of the invention, it is often necessary, when hydrophobic comonomers are employed, to maintain the proportion of the hydrophilic monomers employed above at least about 65 percent of the total combined monomers in order to insure water solubility in the resulting copolymer.

The polymeric polysulfonium additives of the invention can be either linear or lightly cross linked. Their molecular weight is not critical with regard to operability as some benefit is obtained in accordance with the invention with polymeric polysulfonium additives having molecular weights as low as about 1000. Higher molecular weights, however, such as may be obtained in lightly cross-linked polymers so long as they are not so highly cross linked as to be water insoluble, are preferred.

The linear polymeric polysulfonium additives can be directly prepared by homopolymerization of an ar-vinyl-aralkyl sulfonium compound or by copolymerizing at least one such ar-vinyl-aralkyl sulfonium compound with one or more ethylenically unsaturated monomers by any convenient method such as those conventionally employed to polymerize the free radical catalyzed vinyl systems. For this purpose, mass, emulsion or solution polymerization techniques employed in conjunction with such polymerization initiating means as actinic light, ultraviolet radiation, gamma radiation, "azo" catalysts and peroxides are adaptable with such modifications as are necessary